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June 29 to September 28, 1963

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Fifth Quarterly Report
NASA
Goddard Space Flight Center
Contract NAS-5-2860
ESB Report No. 7054.5

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I. INTRODUCTION

This is the Fifth Quarterly Report, covering work done during the period June 29, 1963 through September 28, 1963 on Contract NAS-5-2860 which was awarded to The Electric Storage Battery Company by the National Aeronautics and Space Administration, Goddard Space Flight Center, on June 28, 1962.

II. WORK ACCOMPLISHED DURING THE REPORTING PERIOD

A. Cellophane Degradation

The hydrolysis of cellophane in 31% KOH-ZnO saturated under nitrogen and under oxygen was discussed in the previous report. Under nitrogen there was no appreciable change in the degree of polymerization after 72 hours. Under oxygen, however, the degree of polymerization fell rapidly.

To examine concentration effects of the alkaline solution on the depolymerization of cellulose, hydrolysis experiments were run using 40% KOH-ZnO saturated. Samples of cellophane 8 1/2 in. by 4 in. were suspended on a Teflon frame and immersed in a resin kettle filled with 40% KOH-ZnO saturated. Oxygen was bubbled through the solution and samples were removed at various times. Solution viscosity tests were run and the degree of polymerization calculated. The folloing table compares the results of this experiment with the results using 31% KOH-ZnO saturated.

TABLE I
Cellophane Hydrolysis with Oxygen at 50°C

Time in Hours	31% KOH-ZnO Saturated	40% KOH-ZnO saturated
0	520	520
24	342	337
48	262	290
72	214	240

These results indicate that the effect of concentration is completely overshadowed by the oxidation effect.

In July 1962, samples 3 in. by 2 in. of cellophane PUDO-300 were placed in sealed tubes containing a potassium hydroxide solution. Each sample was placed in a tube and covered with 25 ml of either 25% or 40% KOH. The end of the tube was sealed off leaving approximately 15 cc of air above the surface of the solution. The tubes were placed in large containers and stored at room temperature. During this reporting period, samples were removed from the tubes and solution viscosity tests were run. The average degree of polymerization of the cellophane samples immersed in 40% KOH was 481 units. The average degree of polymerization of the cellophane samples immersed in 25% KOH was 425 units. This constituted a decrease from the original DP (520) of 40 units in 40% alkali and 95 units in 25% alkali. In concentrations of alkali greater than 12%, cellophane will swell appreciably, and as the concentration of alkali increases, the degree of swelling will pass through a maximum and then level off. The literature[1] reports that the maximum degree of swelling of cellulose occurs in 26-33% KOH. The degradation of cellophane occurred faster in 25% KOH because greater swelling increases the amount of internal surface of the cellulose molecule, making it more susceptible to alkali attack. This demonstrates the effect of concentration with a limited supply of oxygen, at room temperature, over a long period of time.

B. Cellophane Modifications

1. Grafting with Vinyl Monomers

In the previous report, preliminary experiments were initiated to graft olefin polymers onto cellulose molecules in an attempt to in crease the resistance of cellophane to oxidation. In those experiments, especially in the case of the methacrylic acid monomer, polymerization was not confined to the grafting sites and homopolymerization of the monomer occurred in the solution. During this reporting period, experimental conditions were modified to control the polymerization reaction, and various other monomers were used to evaluate the effect of grafting onto cellophane.

In the grafting procedure, after the cellophane films have been treated with .1% $FeSO_4 \cdot NH_4 (SO_4)_2$ solution and 1% H_2O_2 solution, and introduced into the monomer solution, 1 ml H_2O_2 was added to initiate polymerization. It was found that by eliminating the peroxide addition no homopolymerization occurred. Experiments were run to determine the effect of time and monomer concentration on the weight increase of the cellophane films. From the following results, it appears that the length of time the film is in contact with the monomer solution is the critical factor.

TABLE II
Percent Wt Increase During
Grafting with Methacrylic Acid

Time in Min.	Monomer Concentration		
	1%	2%	4%
10	0	4	3
20	0	4	6
30	1	8	12
40	3	13	17
50	-	17	24
60	7	25	31
70	-	31	-

By extending the time of contact of the cellophane film with the monomer solution, a graft of styrene and acrylonitrile (2 parts styrene to 1 part acrylonitrile), using the redox system, was obtained; this amounted to a 100% weight increase over the original weight of the cellophane. ~~The percent weight loss during permanganate~~ oxidation amounted to 34%, a reduction of approximately 30% over unmodified cellophane. However, the electrical resistance had been increased from .0088 Ω /in.^{2} for unmodified cellophane to .456 Ω /in.^{2} for the grafted film. Grafting in this manner protects the cellophane against oxidation, but causes a considerable increase in electrical resistance. Grafts amounting to a weight increase of 100% or more were also obtained using styrene and isopropylacrylamide monomers.

In grafts amounting to 60-100% weight increase over the original weight of the film, the weight loss during permanganate oxidation ranged from 30-40%. The weight loss during oxidation seemed to be independent of the weight increase due to grafting.

Very small weight increase (2-9%) during grafting was obtained using N-vinyl-2 pyrrolidone, ethylene imine, and N, N-diethylaminoethyl methacrylate. No substantial weight increase could be obtained using these monomers, even by varying the reaction conditions.

Whenever a substantial weight increase was obtained by grafting, the cellophane was protected from oxidation to some degree. However, this protection was gained at the cost of increased electrical resistance as well as increased embrittlement of the cellophane film.

2. Treatment with Antioxidants

Cellophane 300 PUDO has been treated with several antioxidants to improve its resistance to alkaline oxidation. Samples of cellophane are first swelled in distilled water; they are then immersed in a 10% solution of the antioxidant dissolved in dimethyl formamide. The samples are left in contact with the solution for 48 hours and after soaking, they are air dried. Oxidation tests in alkaline $KMnO_4$ are made on the samples, and the percent weight loss determined. It was observed with two antioxidants, meta- and para-phenylenediamine, that, if after drying, they were placed in an oven for 8 hours at 50°C, the oxidation resistance was remarkably improved. This added curing process did not seem to improve the properties of the other antioxidants tested to date. The following table summarizes the results of these experiments.

TABLE III
Percent Weight Loss in $KMnO_4$ at 25°C

Sample	Air Dried	Conditioned at 50°C for 8 Hrs
Cellophane 300 PUDO	63	65
Cellophane 300 PUDO m-phenylenediamine	65	6
Cellophane 300 PUDO p-phenylenediamine	63	7
Cellophane 300 PUDO m-nitrophenol	59	68
Cellophane 300 PUDO 1- naphthylamine	51	59
Cellophane 300 PUDO N-phenyl-2-naphthylamine	51	59
Cellophane 300 PUDO di-tert-butyl-p-cresol	50	55
Cellophane 300 PUDO n-tetradecyl mercaptan	55	75

The majority of antioxidants slightly improve the oxidation resistance of cellophane. However, both meta- and para-phenylenediamine remarkably improve the oxidation resistance of cellophane. Another advantage of incorporating these diamines into the cellophane is that there is very little change in the electrical resistance of the treated cellophane, compared with the untreated sample. Untreated cellophane has an electrical resistance of .009 ohms/in.^{2} Cellophane treated with meta- and para-phenylenediamine has an electrical resistance of .010 ohms/in.^{2} In effect, we have a film which will not oxidize in alkaline permanganate yet has an electrical resistance comparable to that of cellophane.

3. Phosphorylation

Phosphorylation of cellulose has been reported repeatedly in the literature but all published work dealt either with the flame-proofing of cotton fabrics, or with phosphorylation of cotton linters for the purpose of preparing ion exchangers[2]. No reference to the phosphorylation of cellophane was found.

Samples of cellophane PUDO-300 were immersed for 5 to 30 minutes at room temperature in baths, containing varying proportions of phosphoric acid and urea. The samples were blotted between filter paper and cured for varying lengths of time (from 5 to 30 minutes) at oven temperatures ranging from 105 to 140°C. The cured samples showed weight increases of 40 to 60%, depending on the time of immersion. They were invariably brittle when bone-dry but quite flexible after exposure to atmospheric moisture. They charred but did not ignite when exposed to a flame.

Electrical resistance in 40% KOH was 0.225 ohms/sq. in. initially, but dropped to 0.125 ohms/sq. in. after 10 minutes. However, on prolonged immersion in the electrolyte, all phosphorylated membranes - even those treated under the mildest conditions - disintegrated. Thus, phosphorylation did not seem to hold any promise.

4. Impregnation with Urethane Prepolymers

a. Adiprene L-100 (E. I. duPont de Nemours and Co.), a liquid polyether-urethane polymer with 4% free NCO groups, was used. The liquid polymer was emulsified by the procedure of Berger and Gelbert[3]. The resulting latex was spread on a sheet of cellophane PUDO-300, previously taped to a glass plate. The cellophane wrinkled; it was put with its support in a hot air oven. After 10 minutes cure at 100°C, the coated surface was still tacky, the cellophane had split along several parallel lines, in the machine direction.

Other cellophane samples were coated by dipping in the latex and cured (10 minutes at 100°C). A good, tack-free surface resulted. A check of the electrical resistance in 40% KOH gave the following results:

after 1 min. immersion	220.5 ohms/sq. in.
after 30 min. immersion	6.5 ohms/sq. in.

It appears therefore that the urethane film was somewhat porous though the porosity was obviously small; untreated cellophane gave .009 ohms/sq. in. after 30 min. immersion. The oxidation resistance of the cellophane was improved by the urethane coating but the oxidation loss (in $KMnO_4$) still amounted to 33.1%.

b. Castomer (Isocyanate Products Inc., Wilmington, Del.), isocyanate terminated polyurethane, was used as a 20% solution in ethyl acetate. The coated samples were steam-cured (45 minutes at 110°C). Electrical resistance in 40% KOH gave the following data:

after 1 min. immersion	98.0 ohms/sq. in.
after 30 min. immersion	7.1 ohms/sq, in.
after 17 hrs immersion	0.6 ohms/sq. in.
after 144 hrs immersion	0.1 ohms/sq. in.

On visual inspection of the tested sample it appeared that the urethane coating had become detached from the cellophane. It seems therefore that the urethane polymer had formed coatings on the surface, rather than penetrating into the cellophane.

5. Impregnation with Di-isocyanates

Since preformed urethane polymers had apparently not reacted with the cellulose, reaction of the cellulose with diisocyanates was tried next. A procedure developed for the upgrading of cotton cellulose at Southern Regional Research Laboratory USDA [4] was used.

Tolylene diisocyanate 80/20 (80% 2, 4 -, 20% 2, 6-isomer) was dissolved in freshly dried and distilled pyridine. Surprisingly, a strongly exothermic reaction ensued, whether or not a catalyst (dibutyltin diacetate) was added. The mixture which reached a maximum temperature of 47°C was poured over pre-dried cellophane strips, con tained in a wide glass tube, provided with a drying tube ($CaCl_2$) and thermometer. The reaction tube was placed in an oil bath which had been pre-heated to 100°C. After 10 minutes at 100°C, the cellophane was removed from the tube and washed successively with hot alcohol, hot acetone and water. The cellophane had broken up into several pieces; some of these were sufficiently large for electrical resistance measurements, with the following result:

after 1 min. immersion	0.09 ohms/sq. in.

Resistance did not change after extended immersion but after 100 hours, the samples showed signs of peeling. Delaying addition of the reaction mixture to the cellophane, until after the original reaction had subsided, did not seem to change the outcome.

Greatly improved results were obtained when the following procedure was followed:

The cellophane samples were dried two hours at 105°C, cooled in a desiccator and then immersed for 2 minutes, at room temperature, in a 10% solution of the diisocyanate in dimethyl formamide. They were then treated in one of three ways:

a. The samples were placed immediately in an oven at 105°C. After 10-20 minutes, these samples were tack-free and perfectly transparent but showed round or elongated streaks ("Schlieren").

b. Other samples were hung up in air at room temperature. Turbidity developed after a while, as the isocyanate reacted with the moisture of the air. After 10 to 20 minutes - when the turbidity did not appear to increase any further - the samples were placed in an oven for 10 minutes at 105°C to dry and cure. The samples were completely tackfree, flexible and quite opaque.

c. A third group of samples was dipped, hung up in air and left overnight at room temperature. The oven cure was omitted. These samples were tackfree, opaque and flexible. They were indistinguishable from those of group b.

Samples of all three groups showed weight increases of around 7.5% over untreated cellophane. Immersed in 40% KOH for one week, they appeared intact; there were no signs of peeling.

Electrical resistance measurements, after 1 hour's immersion in 40% KOH, gave values between 17 and 27 milliohms - sq. in. (compared with 10 milliohms for untreated cellophane). The oxidation resistance was somewhat improved over that of untreated cellophane; the oxidation loss was reduced from 63% (for an untreated sample) to 44% (for an opaque sample, resin add-on 7.21%). The tensile strength was increased from 12 lbs. for an untreated sample to 17 lbs. for treated cellophane.

Further tests with isocyanate-treated cellophane are under way. While the results so far appear favorable, it will be necessary to obtain a further improvement in oxidation resistance. An increase in resin pick-up will hardly be desirable because it is likely to cause an undue increase in electrical resistance. A more promising approach seems to be a combination of the isocyanate treatment with antioxidant impregnation.

6. Silver Treatment

Our previous work had shown that silver treated sausage casing had the lowest electrical resistance of all separator materials that had been tested. The oxidation resistance had been improved over untreated sausage casing but still remained unsatisfactory. The question arose whether the results of the silver treatment could be improved by different methods. A recently published patent (U.S. 3,091,554)[5] disclosed a method whereby cellophane is first treated with a silver salt solution and then with sodium borohydride. This method seemed particularly attractive because it offered the added possibility of protecting the end groups of the cellulose molecule through the reducing action of the borohydride.

To investigate these possibilities, samples of cellophane PUDO-300 were treated in different ways so as to obtain deposits of finely divided silver in a cellulose matrix.

a. Samples were immersed 30 min. at 80°C in a bath containing 1% $AgNO_3$ and 0.6% sodium acetate, then washed and dried. The Ag content of the film was 1.9%, the oxidation loss 75%.

b. Samples immersed as before, in a bath containing 1% $AgNO_3$ and 1% sodium acetate. Crystals which formed in the solution were identified as CH_3COOAg. It seems therefore that silver acetate is the species from which Ag is deposited in the film, if the procedure of U.S. Patent 3,013,099[6] is followed. The silver content of the film was 4.1%, oxidation loss, 65%.

c. Samples were immersed in a 1.6% $AgNO_3$ solution at room temperature, followed by 2 hours in 1.6% $NaBH_4$ solution, at room temperature, as disclosed in U.S. Patent 3,091,554 (Rosser et al.); silver content of the film 1:1%, oxidation loss, 69%.

d. Samples were immersed in a solution containing 1% $AgNO_3$ and 0.6% CH_3COONa (30 min. at 80°C); then immersed for 2 hours in 1.6% $NaBH_4$. This combines the treatments disclosed in both above mentioned patents. The Ag content was only 0.51%, the oxidation loss 62%.

e. A sample immersed in a solution containing $AgNO_3$ (1%) alone, showed only weak discoloration; pH = 5.08. A few drops of 26% ammonia were added to raise the pH to 7.5. A strong deposit of silver appeared now in the cellophane. Silver content 5.5%, oxidation loss 68%.

f. Samples immersed for 30 min. in 1.6% $AgNO_3$ at 80°C, rinsed, then steeped at room temperature in a 10% formaldehyde solution, washed and dried, showed a silver content of 6.1%, oxidation loss of 67%.

g. A sample was similarly treated with $AgNO_3$, then immersed in a 1% hydrazine solution (1 hour at room temperature), washed and dried; silver content 4.0%, oxidation loss, 58.0%.

The silver content of the treated cellophane proved to be difficult to control. The highest silver content was obtained by the after-treatment with formaldehyde (6.1% Ag); treatment with ammoniacal $AgNO_3$, without any after-treatment, produced the second-highest Ag content (5.5%). No correlation between silver content and oxidation resistance was obtained; nor was there any evidence that the presence of silver had any definite effect on the oxidation resistance of cellophane.

C. Oxidation Tests

Oxidation tests were run on cellulosic materials using $KMnO_4$ in an alkaline medium at two temperatures. Tests were also run on two additional Permion materials submitted by Radiation Applications Incorporated, Long Island City, New York. The results are summarized in the following table.

TABLE IV
Percent Wt Loss in $KMnO_4$

Material	25°C	50°C
Permion 600 Cellulose	27	41
Cellophane 600 PUDO	63	75
Fibrous Casing	32	38
Permion 1000 (15 mΩ) Teflon	-	19
Permion 1000 (40 mΩ) Teflon	-	8

D. The PMA Membranes

The appended tables V through X contain some hitherto unreported data on the electrolyte absorption and retention, the electrical resistance and dimensional changes of a class of separator materials, designated as PMA.

These membranes have been prepared in this laboratory by a variation of the process, disclosed in U.S. Patent 2,965,697[7]. They were made by impregnating a microporous polyethylene sheet, approximately 0.003 in. thick, with a mixture of methacrylic acid and divinylbenzene, with benzoyl peroxide as catalyst. The relative proportions of methacrylic acid: divinyl benzene are indicated by the suffixes 80/20, 83/17 and 95/5. The mixture was polymerized in situ by a heat treatment. The carboxyl groups were then converted into the salt form, by treating the membrane for 15 minutes with a 27% aqueous KOH solution at 90°C.

The resulting membranes differ from other types of separator materials in that they are substantially non-porous (in the unsolvated form). The pores which were originally present in the carrier (the polyethylene sheet) are now filled with the methacrylate-divinylbenzene copolymer. Particles of electrode material, even if of colloidal dimensions, can therefore not migrate through the membrane, yet the copolymer, being a polyelectrolyte by virtue of its polar carboxyl groups, offers relatively little resistance to the electric current.

The purpose of the divinylbenzene is to act as a crosslinking agent and thus to stabilize the polymer against the action of the battery electrolyte.

The electrical resistance data (Table VI) show that the electrical resistivity of these materials is in the range of other non-cellulosic materials. As expected, the material with the lowest degree of crosslinking (No. 17, PMA 95/5) has the lowest resistivity because it has the highest proportion of polar groups.*

The electrolyte absorption and retention data for the PMA membranes (Table VII) are lower than those for the cellulosic separators but they are higher than those for other non-cellulosic materials reported earlier.

Tables VIII through X, showing the dimensional changes on prolonged immersion in electrolyte, present a pattern which differs from most other materials; there is a rapid increase of around 15% in length and in width but no further changes after this initial increase. The thickness shows essentially no change at low temperature (-26°C) up to 7 weeks immersion. At room temperature, there is no change during the first four weeks and only a moderate increase (12% in thickness after that. At 90°C, the thickness increases initially by 20% and reaches a 50% increase only after 4 weeks. It is worth notin g that these experiments could

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* The data in the 2nd Quarterly Report (p. 22) did not show this effect but a recheck proves that this expected effect does in fact exist; see Table VI of this report.

be carried on for seven weeks, even at 90°C, while many of the other materials had deteriorated to such an extent that their dimensions could no longer be tested even after three weeks immersion.

This stability in electrolyte is borne out by the fair resistance to alkaline oxidation. The oxidation loss in the permanganate test amounts to around 10% (at 50°C for 1 hour).

In one respect, however, these membranes leave much to be desired; their tensile strength is of a very low order, only around 3 lbs. wet tensile (see 3rd Quarterly Report, p. 4).

However, it must be borne in mind that these membranes represent only one embodiment of their method of preparation. This method is capable of many variations. The matrix as well as the polyelectrolyte may be varied. (Tensile strength will also depend on the degree to which polymerization is carried.)

The purpose of this detailed discussion was merely to show the possibilities such a system offers for the development of a better separator material.

E. Diffusion and Reaction of Silver Ions in Separators

In the procedure described in the Fourth Quarterly Report, both compartments of the diffusion cell were filled with 31% KOH (saturated with Ag_2O) after the separator had been clamped between them. One microcurie of Ag 110 in the form of $AgNO_3$ solution was then added to one compartment and the rate of diffusion was measured by determining the build-up of radioactivity in the other compartment. The preparation of the tracer solution has been changed since it was not known how much time was required to reach equilibrium in the exchange reaction between the radioactive silver cation which was added, and the silver in the anion produced when Ag_2O dissolves in alkaline solution. It is the latter species which is present in the electrolyte of alkaline silver batteries. The tracer solution is now prepared by precipitating radioactive Ag_2O directly in the 31% KOH used for diffusion measurements. The quantity of Ag_2O is more than sufficient to saturate the solution. The solubility of Ag_2O in 31% KOH at 25°C was calculated from the results of Amlie and Ruetschi [8] to be 2.2×10^{-4} mol/liter or 51 mg/liter. The amount of Ag_2O precipitated in preparing the tracer solution was 83 mg/liter.

The radioactive Ag 110 solution used had a specific activity of 10 microcuries/ml and consisted of a solution of 2.7 mg $AgNO_3$/ml in N HNO_3. Eight (8) ml of the Ag 110 solution (80 microcuries) was added to a solution of 0.179 g $AgNO_3$ in 10 ml H_2O. The combined solution, containing a total of 0.200 g $AgNO_3$, was added slowly, with stirring, to 1800 ml 31% KOH. Stirring was continued and samples of the solution were withdrawn at intervals and counted. The solution activity did not increase after three days and the solution was assumed to be saturated with Ag_2O. The Tyndall effect was observed in the solution; the amount of colloidal Ag_2O is believed to be a small fraction of the total Ag_2O in solution. The final specific activity of the tracer solution was approximately 0.03 microcurie/ml (20,000 counts/min./ml) or a total of 54 microcuries. The balance of the 80 microcuries was contained in the Ag_2O which remained in excess after the solution was saturated.

F. Diffusion of Dissolved Ag_2O through Separators

The tracer solution was transferred directly to the radioactive compartments of diffusion cells in which the other compartment was filled with 31% KOH saturated with stable Ag_2O. The separators which were tested are listed below:

Cellophane - duPont PUDO-300
Fibrous sausage casing - Visking
Silver treated sausage casing - Avisco
PMA 80/20
PMA 83/17
PMA 95/5
Permion 300

The results of the diffusion measurements are summarized in Figs. 1 and 2 for the PMA and Permion 300 membranes only. The rate of diffusion of dissolved Ag_2O through cellulosic material was so small (because of chemical reaction with the separator) that the counting rate of the solution samples from the non-radioactive compartment was only about 110% of the detector background and the probable error of the measurement was very large. As an example, the results of a two-week diffusion experiment with cellophane (duPont PUDO - 300) are given below. The counting rate of the solution in the non-radioactive compartment is tabulated as determined at various stages of the test.

Diffusion Time hr.	Solution Activity in Non-Radioactive Compartment counts/min./ml
0.25	16 ± 6 *
24	20 ± 6
47.5	15 ± 7
72	17 ± 6
101	16 ± 6
126	11 ± 6
148	15 ± 6
168	17 ± 6
336	12 ± 6

* Percent probable error of individual sample and background determinations was ± 2% at the 0.95 confidence level.

The two sausage casing samples gave similar results in the diffusion test.

It is difficult to select a "best" PMA membrane on the basis of the diffusion test results in Fig. 1, except that the final set of points after 300 hours would indicate that the sample with least crosslinking (95/5) allowed the greatest amount of diffusion to occur. The maxima in the curves were due to loss of activity by adsorption on or reaction with the walls of the cell.

The diffusion of dissolved Ag_2O through Permion 300 (Fig. 2) was quite rapid and again a maximum was present in the activity-time plot. The reason for this behavior is apparent from other data obtained in this test. The rate of loss of solution activity in the radioactive compartment was also measured and is shown as curve A in Fig. 3. After the test had proceeded about 15 hours, the rate of decrease of solution activity with time was constant for the remainder of the test. Results given in the next section of this report show that Permion

300 does not react with dissolved Ag_2O. Therefore, neglecting the diffusion of a few percent of the radioactivity originally present, the loss of solution activity must be ascribed entirely to reaction or adsorption on the cell walls. When the cell contains a cellulosic separator which does react rapidly with dissolved Ag_2O, the rate of loss of solution activity in the radioactive compartment takes the form of curve B in Fig. 3 which was obtained in the tests of fibrous and silver-treated sausage casing. The initial slope is much greater because the radioactive silver species is being removed from solution by reaction with both the cell walls and the separator sample. Since these same processes occur in the other compartment of the cell, diffusion measurements on cellulosic separators are difficult to obtain and interpret.

G. Reaction of Dissolved Ag_2O with Separators

Since it was not possible to obtain diffusion measurements for cellulosic materials because of their affinity for dissolved silver, it was decided to determine the rate and extent of this reaction with such separators. Preliminary results indicate large differences in the rate of this reaction among materials of various types.

The procedure used to measure the rate of reaction of separator material with dissolved Ag_2O was as follows. A 0.25 g separator sample, previously equilibrated in 31% KOH, was placed in 200 ml of the tracer solution (described above) in a 1 liter beaker which contained a Teflon-coated stirring bar. The solution was maintained at a constant temperature of 28°C. Stirring was begun at the time the separator sample was added to the solution and was continued for the duration of the experiment which was usually not more than 24 hours. The tracer solution was 31% KOH saturated with radioactive Ag_2O. The dissolved Ag_2O content of 200 ml of this solution was 10 mg. The rate of reaction of the separator with the dissolved silver was obtained by withdrawing 1 ml samples at intervals and measuring the counting rate. The fraction of the original activity remaining after each interval (A/A_0) was calculated. The results are given in Figs. 4 and 5 in which the fraction A/A_0 is plotted vs. time.

The curves in Fig. 4 show that nearly all the dissolved Ag_2O in the tracer solution had been removed in 3 hours by reaction with duPont PUDO-300 cellophane. After 0.8 hr the activity was reduced to one-half the original value. In the course of the test the cellophane became very dark and nearly opaque. The results of two tests with identical samples were in close agreement. Amine treatment of the same cellophane decreased the reaction rate approximately 50%. As shown in Fig. 4, the time required to reduce the activity to one-half the original value was 1.5 hr.

The three PMA membranes were tested in the same way with the results shown in Fig. 5. All appeared to undergo about the same degree of reaction after which the solution activity did not change. The 0.25 g samples apparently had a "capacity" to react with only about 1 mg of dissolved Ag_2O. Also shown in Fig. 5 is the fact that Permion 300 is practically inert in this solution. After 18 hours in contact with this separator the solution retained 99% of its original activity. The dashed line at the extreme left in Fig. 5 shows, for comparison with Fig. 4, the reaction rate of PUDO-300 cellophane.

H. Measurement of Average Pore Size of Separator Materials

The method of measuring the average pore size in separator materials has been fully described in our previous report (see Fourth Quarterly Report, p. 8). The apparatus has been improved over that shown in Fig. 3 of that report without, however, departing from the basic design. The riser tube-meter stick assembly has been replaced by a graduated capillary. The support for the riser tube has also been improved to insure a leakproof fit (by means of a rubber O-ring).

The porosities and pore diameters of some separator materials are listed in the appended Table XI. Porosities are shown both in terms of pore volume per unit area and in percent of the volume.

Pore diameters have been calculated by means of the formula shown in the Fourth Quarterly Report, p. 10. To test the validity of using the term log H/h - which is a measure of the electrolyte flow through the separator - these values were plotted against time. Fig. 6 shows the values for a rapid flow (32.5 cm in approximately 3 minutes); the separator material in this case was Acropor WA. All points lie on a straight line. Fig. 7 gives the corresponding values for cellophane. Although it took almost 350 minutes for the same amount of electrolyte to flow through the cellophane sample, the log H/h values do not deviate too widely from a straight line.

The pore diameters of the various cellulosic materials are all within a fairly narrow range, between 200 and 300 Angstrom units. The only exception is the silvered sausage casing (sample No. 9). The smaller diameter (180 Å) would seem to indicate that the diameter has been somewhat reduced by silver deposition.

The pore diameter of sample No. 19 (microporous polyethylene) is larger by an order of magnitude (2300 Å). However, in the PMA samples (Nos. 15-17), which are based on microporous polyethylene, the average pore size has been drastically reduced by the incorporation of the polyelectrolyte.

All these calculations are based on the assumption that all the pores in the separator materials are cylindrical and go straight through the sheet. Such is, however, not the case. To get a better understanding of the pore structures, it is necessary to obtain a measure of the extent to which the pore structures deviate from the cylindrical shape. We intend to supplement the pore size measurements with tortuosity calculations, and hope to include the pertinent data in our next report.

I. Summary

The cellulosic membranes - cellophane and sausage casings - have been shown to be readily oxidized. Incorporation of amine antioxidants has resulted in a marked improvement of their oxidation stability without raising their electrical resistance.

Nor does treatment with isocyanates cause an undue increase in electrical resistance. The mechanical properties of cellophane are improved but this treatment does not enhance the oxidation resistance.

Diffusion tests have shown that there is substantially no diffusion of Ag ions through cellulosic membranes. The results of these tests indicate that the Ag ions are retained by, and react with, the cellulose. The improved chemical stability of cellulose, due to the addition of antioxidants, is confirmed by the slowing down of its reactivity with dissolved silver.

The reactivity with Ag ions appears to be absent in the plastic types of separators. These show definite rates of diffusion. Permion 300 (a modified polyethylene) showed the fastest diffusion rate of the materials so far tested. That this marked diffusion rate is not merely an effect of the pore size is demonstrated by the PMA's; the fastest diffusion rate within this class is exhibited by PMA 95/5. Its average pore diameter is close to, and in fact somewhat smaller than that of the cellulosic materials, yet PMA 95/5 shows a marked diffusion rate while there is no measurable rate of diffusion through the unmodified cellulosic materials.

Present indications are that cellophane and sausage casing act as effective barriers for Ag ions but that they are consumed in the process. Other materials which were tested were resistant to the chemical action of silver ions but they allowed the passage of these ions, regardless of pore size.

J. Future Work

1. Future work will therefore be directed towards testing the "sacrificial theory" of the action of cellulosic materials, by chemical modification of the cellulose molecule.

2. Preliminary results in the area of protecting cellulosic materials by antioxidants appear promising; other antioxidants will be tried.

3. The investigation of diisocyanate treatment of cellophane will be continued.

4. The impregnation of the chemically inert microporous polyethylene with polyelectrolytes will be extended to polymers other than PMA.

5. Diffusion tests will be completed on the remaining separator materials, and applied to other materials that may become available in the course of our investigations.

6. Our porosity studies will be supplemented by estimations of tortuosity.

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TABLE V

Electrical Resistance(Ohms) in 31% KOH at 26°C
after different soaking time
(Average values for 3 samples-Exposed area: 0.15 sq. in.)

Sample No.	Material	5 min.	10 min.	20 min.	1 hour	24 hour
15	PMA 80/20	0.631	0.603	0.532	0.563	0.564
16	PMA 83/17	0.469	0.458	0.448	0.435	0.417
17	PMA 95/5	0.226	0.221	0.218	0.214	0.198

TABLE VI

Electrical Resistivity in 31% KOH at 26°C

Sample No.	Material	Ro	% Deviation	Dry Thickness in. x 10^{-4}	Dry Thickness cm x 10^{-4}	Wet Thickness in. x 10^{-4}	Wet Thickness cm x 10^{-4}	Change	R_1	ρ
~~15~~	~~PMA 80/20~~	~~0.564~~	~~1.8~~	~~38~~	~~97~~	~~34~~	~~86~~	~~-10.5~~	~~.085~~	~~63.5~~
16	PMA 83/17	0.417	3.0	40	102	40	102	0	.062	39.6
17	PMA 95/5	0.199	1.3	35	89	34	86	-3.5	.030	22.3
	Column No.	1	2	3	4	5	6	7	8	9

Legend:

Column 1: R_O = Observed values (ohms), resistance after 24 hrs. soaking in 31% KOH, exposed area 0.15 sq. in. (average of 3 samples).

Column 2: Average % deviation of the 3 samples of Column 1.

Column 5 and 6: Thickness of separator after 70 hours soaking in 31% KOH.

Column 7: % Change shows swelling (+) or shrinkage (-) of separator thickness

Column 8: R_i = Resistance (ohms for 1 sq. in.) at actual thickness.

Column 9: ρ = Specific Resistivity (ohms - cm).

TABLE VII

Electrolyte Absorption and Retention at 26°C

Sample No.	Material	Dry Weight grams	Dry Thickness cm x 10^4	Dry Volume cm^3 x 10^4	Absorption grams	Absorption g/cc	Retention grams	Retention g/cc
15	PMA 80/20	.1919	97	.1877	.4707	2.51	.1053	.56
16	PMA 83/17	.2566	102	.1974	.3580	1.81	.0618	.31
17	PMA 95/5	.1670	89	.1723	.6746	3.92	.2309	1.34
	Column	1	2	3	4	5	6	7

Legend

Column 1: Dry weight of separator sample.

Column 2: Thickness of the dry separator.

Column 3: Volume of the dry separator.

Column 4: Weight of 31% KOH, absorbed in 70 hours soaking.

Column 5: Weight of absorbed electrolyte per cm^3 of dry separator volume.

Column 6: Weight of 31% KOH, retained after 30 min. draining.

Column 7: Weight of retained electrolyte per cm^3 of dry separator volume.

TABLE VIII

Dimensional changes in 31% KOH at-26°C

Sample No.	Material	70 hours Length	70 hours Width	70 hours Thickness	7 days Length	7 days Width	7 days Thickness	14 days Length	14 days Width	14 days Thickness
15	PMA 80/20	+9	+10	+18	+9	+9	+16	+9	+10	+24
16	PMA 83/17	+15	+14	0	+16	+14	0	+16	+14	+10
17	PMA 95/5	+12	+12	+14	+11	+12	+17	+11	+14	+14

Sample No.	21 days Length	21 days Width	21 days Thickness	28 days Length	28 days Width	28 days Thickness	35 days Length	35 days Width	35 days Thickness
15	+9	+10	+11	+9	+10	+21		discontinued	
16	+16	+14	0	+16	+14	0	+16	+14	0
17	+12	+13	+17	+12	+14	+29		discontinued	

Sample No.	49 days Length	49 days Width	49 days Thickness
15			
16	+16	+14	0
17			

TABLE IX

% Dimensional changes in 31% KOH at +26°C

Sample No.	Material	70 hours Length	70 hours Width	70 hours Thickness	7 days Length	7 days Width	7 days Thickness	14 days Length	14 days Width	14 days Thickness
15	PMA 80/20	+10	+10	-10	+10	+7	+10	+10	+6	+5
16	PMA 83/17	+13	+14	0	+13	+14	0	+13	+14	0
17	PMA 95/5	+13	+15	+23	+13	+14	+20	+13	+14=	+23

Sample No.	Material	21 days Length	21 days Width	21 days Thickness	28 days Length	28 days Width	28 days Thickness	35 days Length	35 days Width	35 days Thickness
15	PMA 80/20	+10	+9	-5	+10	+8	-3	discontinued		
16	PMA 83/17	+13	+14	0	+13	+13	0	+13	+13	+12
17	PMA 95/5	+13	+14	+26	+13	+15	+26	discontinued		

Sample No.	49 days Length	49 days Width	49 days Thickness
15			
16	+13	+13	+12
17			

TABLE X

% Dimensional changes in 31% KOH at +90°C

Sample No.	Material	70 hours Length	70 hours Width	70 hours Thickness	7 days Length	7 days Width	7 days Thickness	14 days Length	14 days Width	14 days Thickness
15		+8	+10	+21	+8	+8	+16	+6	+8	+34
16		+17	+14	+20	+17	+14	+20	+16	+14	+20
17		+12	+12	+17	+10	+12	+14	+6	+9	+37

Sample No.	Material	21 days Length	21 days Width	21 days Thickness	28 days Length	28 days Width	28 days Thickness	35 days Length	35 days Width	35 days Thickness
15		+5	+8	+25	+4	+6	+37			
16		+16	+14	+20	+15	+14	+50	+15	+11	+50
17		+7	+9	+23	+7	+8	+17			

Sample No.	49 days Length	49 days Width	49 days Thickness
15			
16	+15	+11	+52
17			

TABLE XI

Porosity in 31% KOH

Sample No.	Material	Total Porosity $(cm^3/cm^2) \times 10^{-3}$	%	Average Pore Diameter $(cm\text{-}sec) \times 10^{-8}$
1	Celloph. PUDO-300	9.1	>90 *	200
2	Celloph. PUDO-600	11.3	>90 *	400
7	Saus. Casing	14.3	70	450
8	Fibr. Saus. Casing (Avisco)	15.5	34	300
9	Silvered Saus. Casing (Avisco)	16.6	70	180
15	PMA 80/20	4.6	56	300
16	PMA 83/17	6.3	63	350
17	PMA 95/5	8.0	64	300
19	Mipor (Polythene)	6.7	50	2300
24	Fibr. Saus. Casing	16.8	83	450
25	Cellop. MPDA impreg.	9.6	> 90 *	225
26	Acropor WA	12.0	75	3200

* The precision of these valves is uncertain due to the nature of cellulosic materials (high degree of swellings in KOH, possible ion exchange effects).

Figure 1
Diffusion of Dissolved Ag_2O through
PMA Membranes

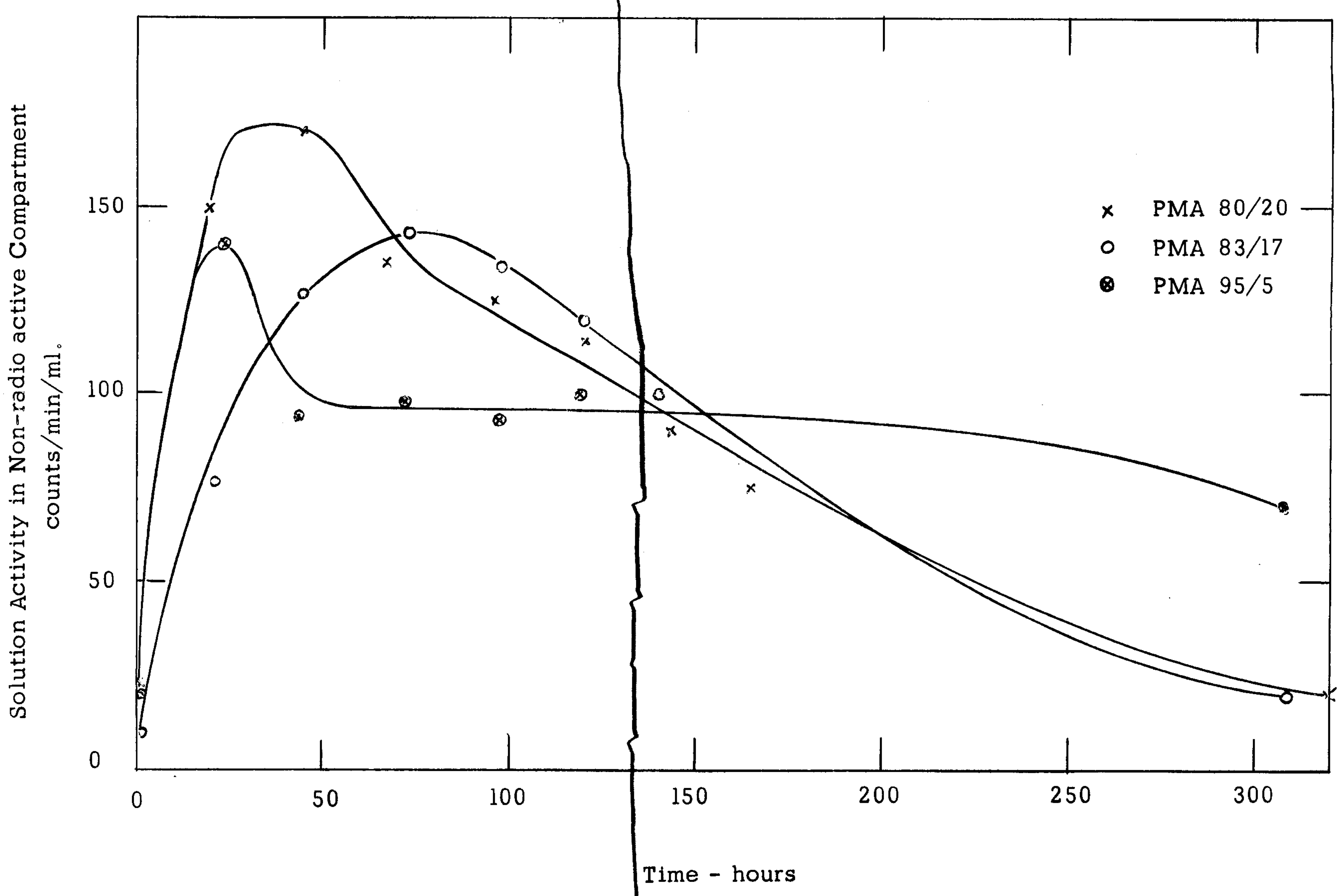


Figure 2

Diffusion of Dissolved Ag_2O through Permion 300 Membrane

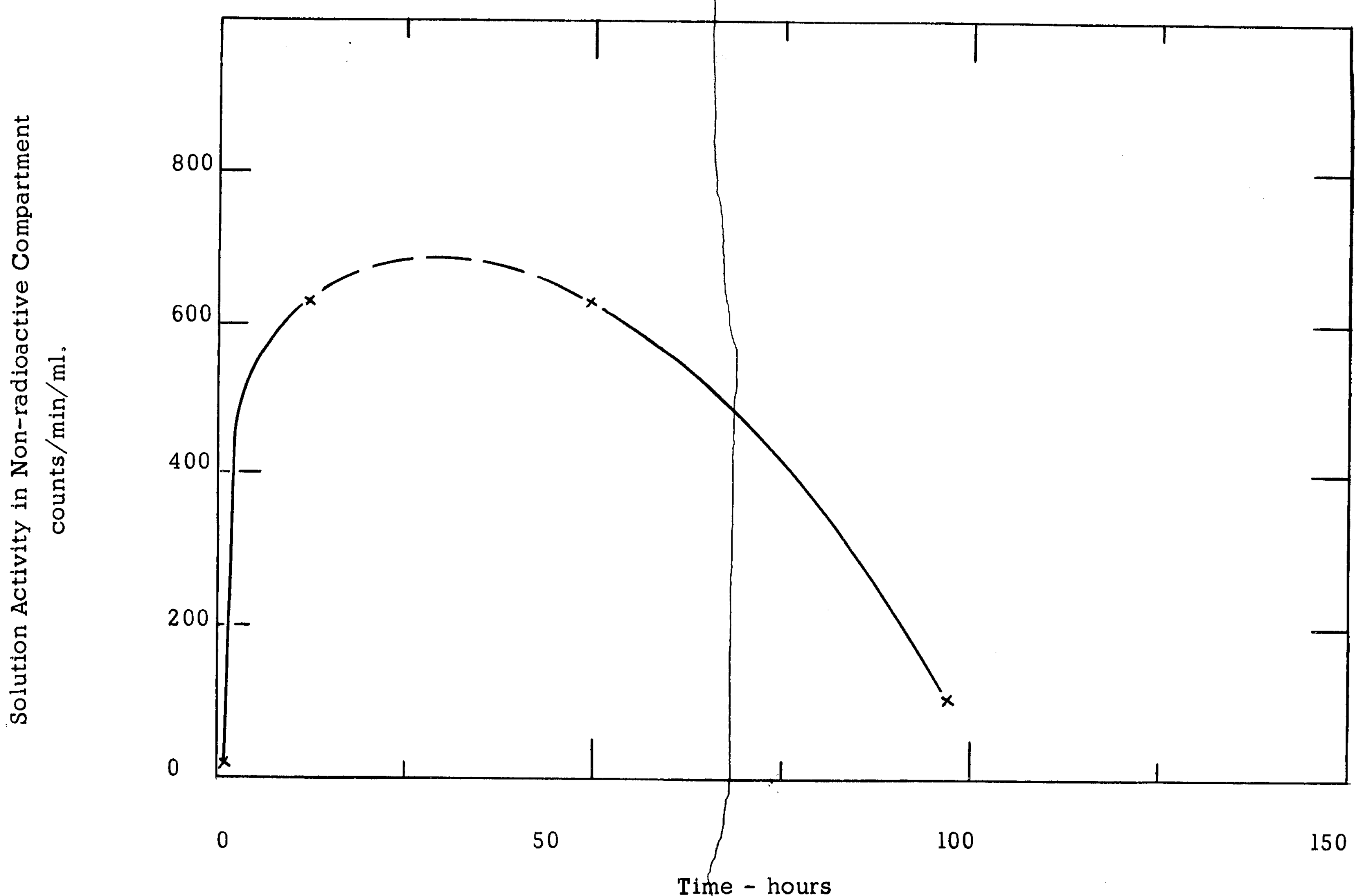
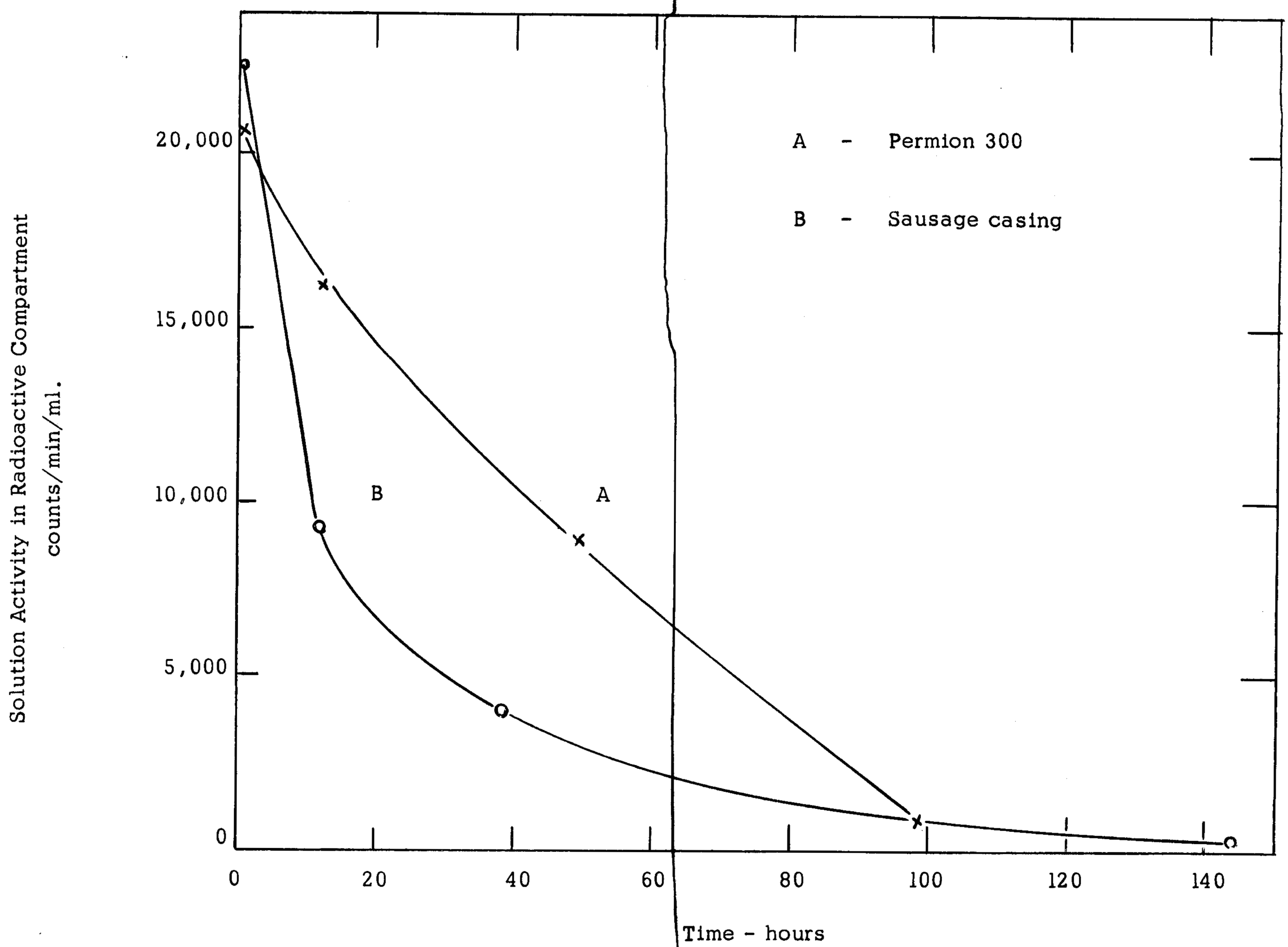
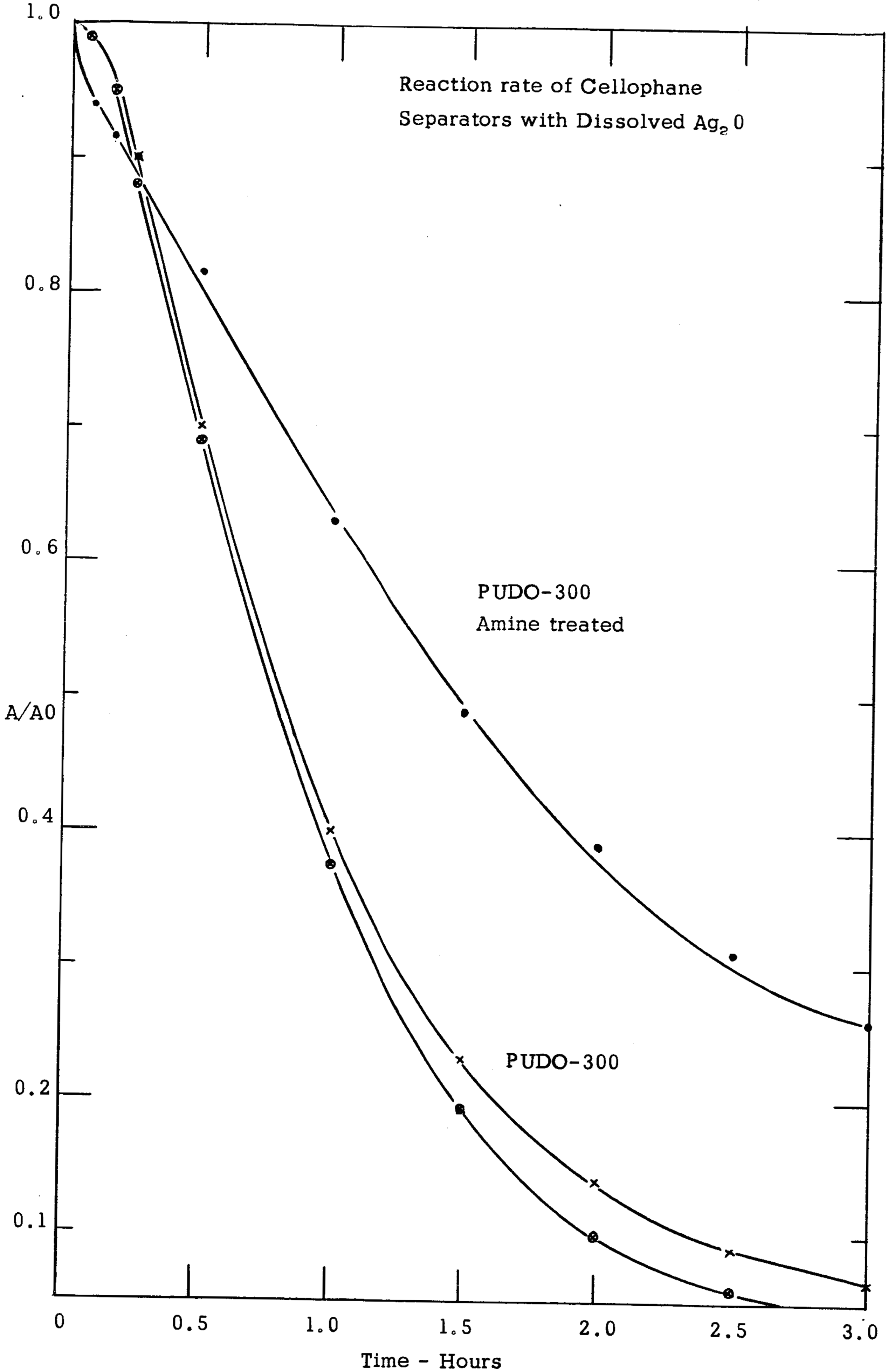


Figure 3

Loss of Solution Acitivty in Radioactive Compartment of Diffusion Cell due to Reaction of Dissolved Ag_2O with Cell Walls and Separator Sample





Reaction rate of Cellophane
Separators with Dissolved Ag_2O
PUDO-300
Amine treated
PUDO-300
A/A0
1.0
0.8
0.6
0.4
0.2
0.1
0
0.5
1.0
1.5
2.0
2.5
3.0
Time - Hours

Figure 4

Figure 5
Reaction Rate of PMA and Permion Membrane
with Dissolved Ag_2O

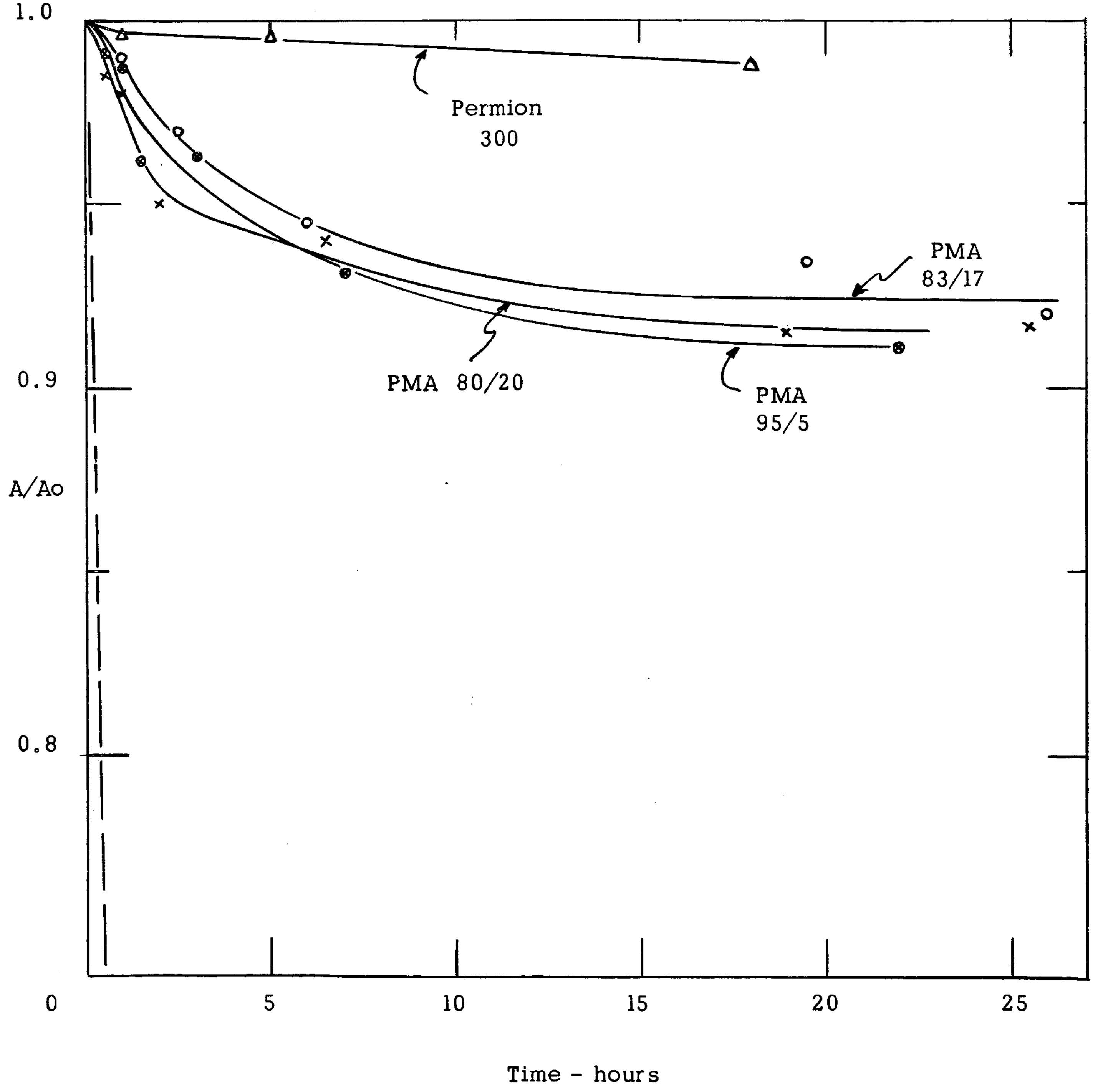


Figure 6

Logarithm of ml Electrolyte vs. time - for Acropor WA

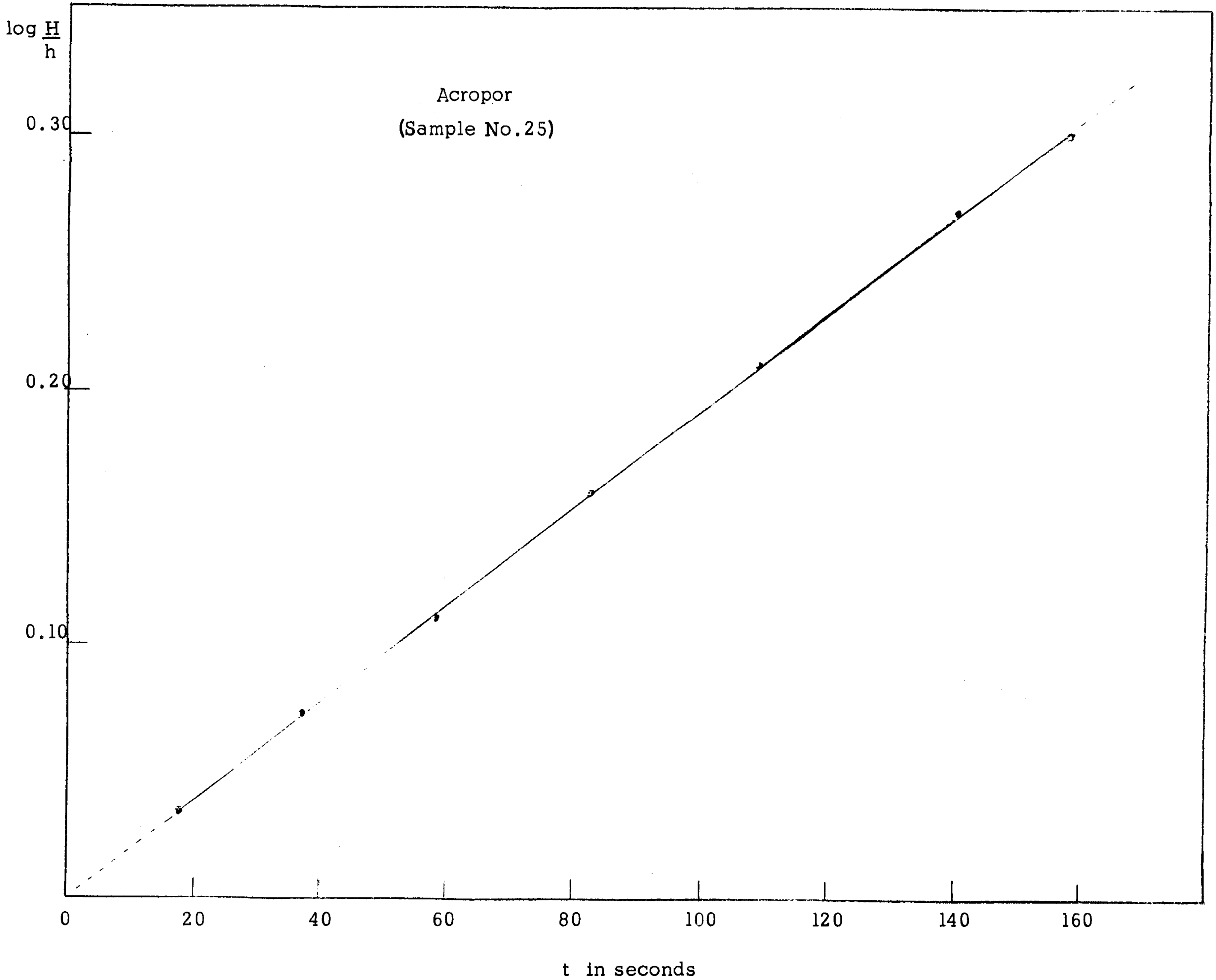


Figure 7

Logarithm of ml Electrolyte vs. time - Cellophane